

Real Time Detection of Sodium in Size-Segregated Marine Aerosols

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LONG-TERM GOALS

Our long range goals for this project are to improve our understanding of: 1) the chemistry and physical properties of seasalt aerosols, 2) the relationship between seasalt aerosol properties and the turbulence that generates them, 3) the effect of seasalt aerosols on the propagation of light through the marine atmosphere, and 4) to develop improved relationships between seasalt aerosol production and remotely observable parameters.

OBJECTIVES

The objective of this project is to develop a new capability for the characterization of marine aerosols. Specifically, we propose to develop the capability to make near real-time measurements on the quantitative chemical composition of individual, marine aerosols of known size. The scientific goal of the work is to investigate the contribution of seasalt to the submicron aerosol mode. We have developed an instrument that has demonstrated this capability for sodium and a prototype has been deployed as part of the ONR-sponsored SEAS campaign. We are attempting to extend this capability to give a simultaneous measurement of the sodium and sulfur content of the aerosol. The ultimate goal of the project is to develop and deploy a field-ready instrument that could carry out the proposed measurements from land based, shipboard or airborne platforms.

APPROACH

Our approach is to introduce individual aerosols into a hydrogen/air flame and to utilize either laser induced fluorescence or emission to monitor the sodium content of aerosols. We have developed an emission based sodium aerosol detector (ASD) that can quantitatively measure the sodium content of aerosols. The ASD can detect particles that contain more than 1×10^{-14} g of sodium, equivalent to an 180 nm diameter dry sodium chloride particle. Particles can be size-segregated prior to analysis using a differential mobility analyzer. This phase of the project had two components a) incorporate design improvements based on the SEAS deployment into the emission based ASD b) incorporate laser induced fluorescence detection of sodium and characterize the detection limits of this technique. The goal is to develop a detector which is sensitive to sub-micron particles, responds linearly to aerosol sodium and sulfur content, and is unaffected by the presence of other chemicals in the particle, such as sulfates, nitrates, ammonia, organic carbon, etc.

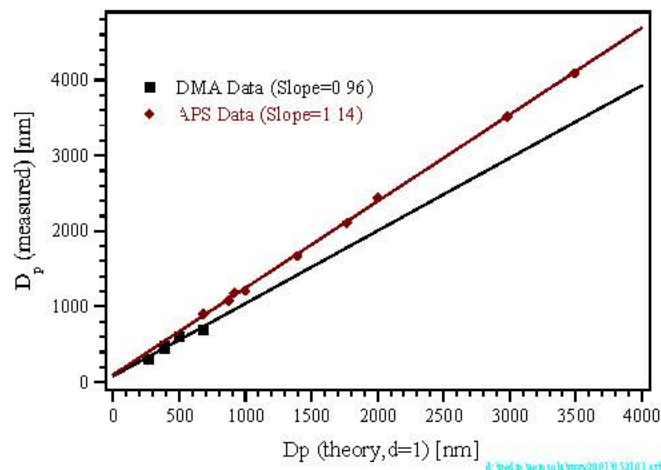
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WORK COMPLETED

The initial field deployment of the ASD was carried out at Bellows AFB, Oahu, Hawaii as part of the ONR-sponsored Shoreline Environment Aerosol Study (SEAS). This work focused on assessing the field reliability and performance of the instrument and its response to ambient marine boundary layer aerosols. Issues addressed during this study included: detection limits, inlet efficiency, coupling of the ASD to particle sizer/counter, and in-field calibration. In order to ensure the integrity of the SEAS data we performed new calibrations and measured the absolute transmission efficiency of ASD as a function of aerosol diameter. Based on our experience during the SEAS deployment we have redesigned and completely rebuilt the emission based ASD. We have implemented 10 kHz, laser induced fluorescence detection of the sodium content of laboratory aerosols. These experiments demonstrate that this approach is feasible for quantitative determination of aerosol chemical composition and, for detection of sodium, leads to at least a two order of magnitude improvement in detection sensitivity over the already impressive emission detection limits.

RESULTS

Generation of well defined monodisperse aerosol is critical for ASD calibration. To increase reproducibility of the VOAG aerosol output a He-Ne laser beam is now focused on the liquid jet, about 8 mm downstream from the vibrating orifice allowing the droplet breakup process to be monitored in real time. All calibration experiments are performed while simultaneously monitoring droplet size. The VOAG has also been modified to run at very high dilution flows and small samples can be drawn into tubes without overpressurizing the detectors and losing most aerosols at the outlet of the VOAG due to turbulence. After many experiments at different frequencies and gas flows combining the modified VOAG with the APS, our understanding of both the initial droplet formation and dry aerosol formation process has improved. Operating within the workable limits (typically 30-90 kHz), there are only selected frequencies where “clean” droplet formation can be achieved. Provided the absorption trace



is

Figure 1: Correlation of the calculated VOAG aerosol sizes with the data measured with the DMA and the APS

clean, the output of the VOAG is always monodisperse and the aerosol sizes measured by the APS change in the expected fashion by changing frequencies and liquid flow. At very high dilution flows, (60 slm, about 20% rel. humidity) the sizes measured by the DMA are now very close to the calculated values (within a few percent).

As theoretical size and measured size could be related to each other, it is possible to compare ASD and DMA size distributions on an absolute basis. The ASD resolution matches exactly the DMA resolution. Examination of the DMA size distributions also sheds light on the past difficulty of matching theoretical and measured sizes. Typically the DMA distributions show multiple peaks which correspond to aerosols which have multiple charges, giving up to 5 daughter peaks. This is due to the fact that VOAG aerosols have a very different charge distribution compared to normal aerosols and therefore neutralization doesn't take place in the usual (TSI planned) way.

The transmission efficiency of the ASD was determined as a function of aerosol size by comparing the ASD count rate with the measured aerosol number density of monodispersed aerosols of various diameters. Figure 4 summarizes the measured transmission ratios. They show that the transmission through a nafion dryer is slightly more efficient. Most likely this is due to the higher "stickiness" of semi-wet particles. It shows that transmission efficiencies are high and relatively independent of diameter below 2 microns.

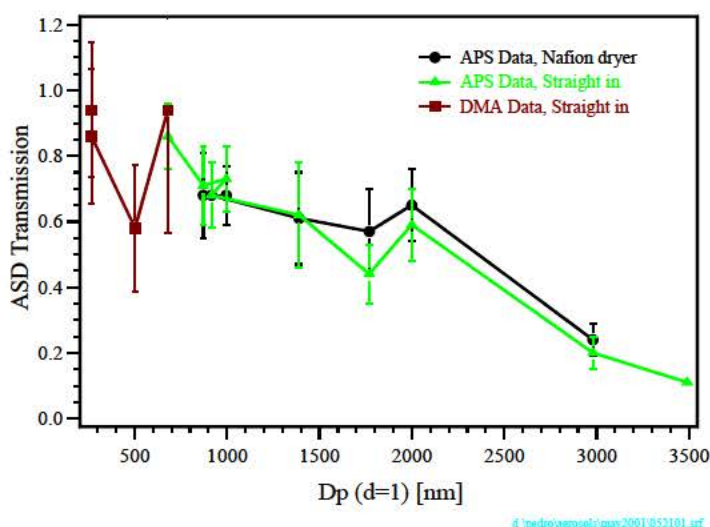


Figure 2: Size dependent transmission ratios for the ASD. APS based data calculated by comparing APS measured aerosol concentrations at the bottom of the VOAG with aerosol counts in the ASD for one injection cycle. DMA data taken by comparing CPC counts at the bottom of the DMA for the peak size of the VOAG spectrum with the average ASD counts for 5 injection cycles.

The SEAS dataset is being reanalyzed on the basis of the new calibration and transmission data. Figure 3 shows an example of a SEAS ASD data set, together with aerosol size distributions measured by an APS on the sampling tower and DMA data obtained before the ASD inlet. Unfortunately the APS, DMA and ASD data were not obtained simultaneously. In addition it is important to remember that the

ASD is only sampling aerosols with diameters less than 3 microns but with no size segregation. In addition the ASD data is expressed as the equivalent diameter of 100% sodium aerosol with a density of 1. Though somewhat limited in scope since it consists only of non-size resolved data, it indicates that most of the particles with diameters greater than 0.3 microns consist of sea salt. In addition the dataset will be valuable for comparison with measurements from Clarke et al. using the heated OPC/cascade impactor.

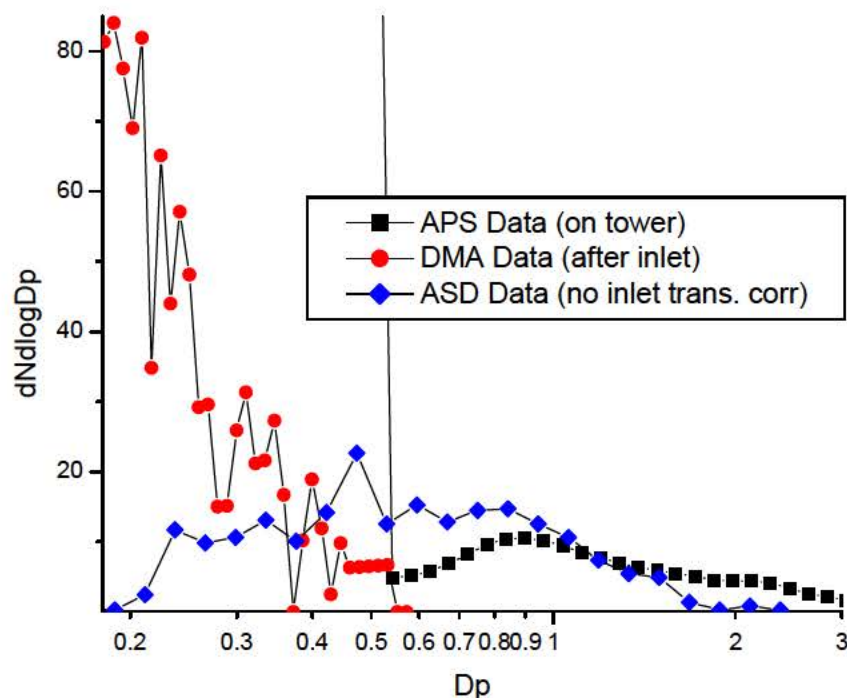


Figure 3. Aerosol size distribution measured using an APS on the SEAS sampling tower, a DMA at the bottom of the inlet compared with the ASD number distribution.

The ASD has been completely rebuilt, including a new burner system, and performance tests are currently underway using both laboratory generated and outside aerosols.

In addition to experiments using emission we have been attempting to implement high repetition laser induced fluorescence (LIF) for quantitative detection of sodium and sulfate. Our initial work has focussed on sodium because the excitation wavelength is in the visible region of the spectrum making it easy to generate with the laser system. In addition the detection uses the same PMT and filters as the emission instrument. The setup for LIF excitation utilizes a high repetition diode-pumped Nd-YLF laser which pumps a micro-dye laser. The lasers operate at a frequency of 10 kHz. The laser wavelength is monitored by a pulsed wavemeter which ensures that the laser is tuned to the center of the Na D-line transition at 589.0 nm. Fluorescence is detected by a PMT and processed by a fast A/D

card. We use the burner and calibration system from the emission instrument. Figure 4 shows the LIF signal associated with the passage of a single, 400 nm diameter, sodium aerosol through the flame. The laser pulses at 10 kHz with a pulse width of 25 nsec, hence the pulses occur every 100 μ sec. The duration of the LIF signal is approximately 50 nsec long and we capture 7 pulses as the sodium plume from the volatilized aerosol passes through the flame. These results indicate that this approach to detection is clearly feasible and that for elemental detection it is extremely sensitive. Based on work so far we estimate that seasalt particles with a dry equivalent diameter of 10-50 nm should be detectable using this approach. Detection of aerosol sulfate will be attempted by monitoring the SO₂ formed in the flame and requires frequency doubling and mixing to generate the 220 nm excitation wavelength,

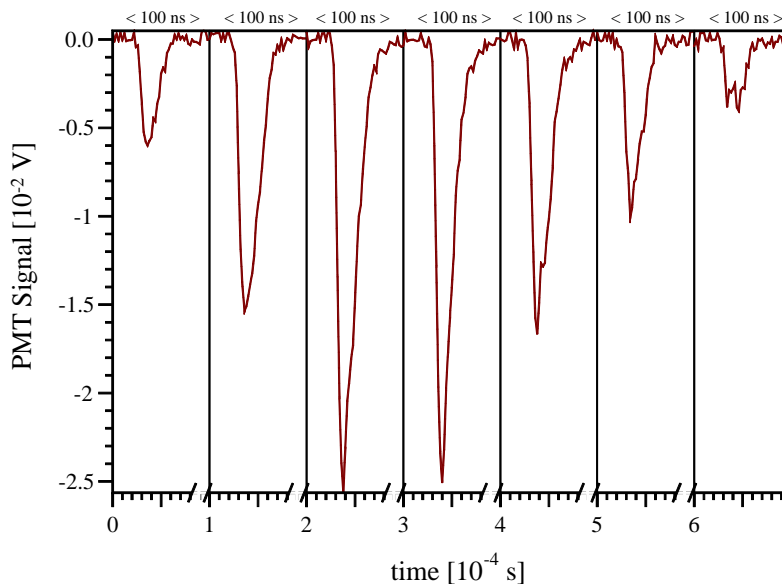


Figure 4. *Laser induced fluorescence signal from a single ~400 nm aerosol passing through the flame. The pulses occur every 100 μ sec hence the bottom axis represents 0.7 msec with axis breaks.*

IMPACT

These results show that quantitative determination of the sodium content of size resolved aerosols is possible using both emission and LIF based detection techniques.

TRANSITIONS

We are in the process of comparing the ASD data with results obtained using a heated OPC by Clarke and coworkers.

PUBLICATIONS

C. D. Clark, P. Campuzano-Jost, D. S. Covert, R. S. Richter, H. Maring, A. J. Hynes, and E. S. Saltzman, Real-Time Measurement of Sodium in Single Aerosol Particles by Flame Emission: Laboratory Characterization, *Journal of Aerosol Science*, vol. 32, 765-778, 2001